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SYNTHETIC LUBRICATING OILS

Nafta [Petroleum], Vol XI,
No 4, April 1955, Stalinogrod,
Pages 86-89

Stanislaw Tertil

A review of the methods of obtaining synthetic lubricating oils, based on CIOS and BIOS data, was presented by Doctor Tokarzewski in this periodical (Nafta, No 8 and 9, 1954). The present writer wishes to add a few comments to this interesting review.

Natural lubricating oils, as defined by the writer, can be obtained from petroleum oil, and other than that only from certain shale oils and from the pretar fractions of brown coal. Just as petroleum oils are divided into oils with a paraffin, naphthene, and asphalt base, so can shale and pretar oils be similarly divided. Lubricating oils can only be made of materials which will, with the application of proper methods, yield oils with similar hydrocarbon structures, as those obtained from petroleum oils.

Certain types of bituminous shale and most brown coals (e.g., lignites) contain large components derived from humus. They yield liquid products which contain primarily aromatic compounds, with large amounts of asphalt, resins, and phenol derivatives ranging from univalent to polyvalent and multiple-ring compounds; the inert hydrocarbons contained in these oils in small amounts also have an aromatic structure with short side chains. It is quite clear that these types of raw materials and their products are not suitable for the production of lubricating oils; they can be used for obtaining driving fuels only (e.g., benzene or naphtha for tractors), or by mixing with a higher grade product they can yield Diesel oils or fuel oils. The pretars are also used for producing driving fuels through hydrogenation.

If high-grade bituminous shale and certain types of brown coal are degasified at low temperatures, liquid products which contain sufficient quantities of heavy oils for technical processing are obtained. These oils have a ring structure and long side chains. They must be subjected to selective refining processes, and because of their high content of compounds with double bonds, they must be subjected to special processes in order to obtain lubricating oils. Petroleum shale which is counted among the bituminous shales, may be suitable for the production of lubricating oils, depending on the type of petroleum oil with which they are saturated.

As far as the Friedel-Crafts reaction and the polymerization of olefins with the aid of $AlCl_3$ is concerned, neither organic sulfur compounds nor H_2S harm either the reaction or the polymer, in the processing of liquid olefins. The sulfur compounds are reduced to hydrogen sulfide by means of atomic hydrogen and escape along with the other gases generated during the reaction. It is possible that in the polymerization of ethylene under a pressure of 80 atm where the H_2S remains locked in the autoclave, the former may have a harmful effect. On the other hand, oxygen links may prevent the reaction from taking place and may make it impossible to obtain the lubricating oils from the olefins. This would depend on the types of oxygen links and on their numbers.

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The German synthetic oils SS906 and SS903 had a viscosity of 2.8 to 5.8 E_o at a temperature of 100°C, which may be seen in the table presented by Doctor Tokaczewski. The figures given in the sources quoted by the author, concerning the amount of catalyst used for polymerizing olefins derived from the Fischer-Tropsch process (10 to 15% $AlCl_3$), and the duration of the process (24 hours) appear to be much too high. The data concerning the yield of oil are also questionable.

If the losses in cracking amount to 5%, the uncondensed olefins to 27% and the oils of category I to 50%, that gives a total of 82%. This would leave only 18% for any polymerization losses and for the oils of category II. This figure is decidedly too low, especially with such a large amount of catalyst used, since the amount of complex compounds (sludge) is directly related to the amount of $AlCl_3$ used. The losses are also related to the duration of the process. Therefore, under the conditions cited by the author, the yield of oils belonging to category I cannot amount to 50% of the paraffin used.

Concerning the condensation of naphthalene with chlorinated paraffin hydrocarbons obtained by the Fischer-Tropsch synthesis, the inventor of this method, Doctor H. Koelbel, published an article on the subject in Erdoel und Kohle (No 10/11, 1948), after the Allied publications. In this article, he gave a number of interesting details and different working conditions from those previously published.

A "kogazyna" [cogazine; a mixture of kerosene, Diesel oil, and paraffin wax used for fuel (Fischer-Tropsch process)] fraction from 280 to 320°C was used for the chlorination; the oils obtained in this way were not subjected to deparaffination. The chlorine content in the chlorinated cogazine amounted to 20%, and was found to depend on the boiling range of the cogazine fraction used. With a cogazine fraction of 150 to 220° the chlorine content amounts to 31%; with a 320 to 340 fraction it amounts to 17.1%. The lower the boiling range of the initial fraction, the poorer the viscosity index and the lower the solidifying point of the polymer. The chlorination temperature is given as ranging from 40 to 120°C.

The effects of the proportions of naphthalene and cogazine are very interesting. H. Koelbel states that 2 reactions occur during the process, namely:

1. the desired alkylation of the naphthalene;
2. the undesirable condensation of chlorocogazine with itself.

Theoretically, 53% of naphthalene is required for obtaining monoalkyl naphthalene. In practice, however, an excess of naphthalene is required in order to prevent the second reaction from occurring and to avoid the production of oils which are less temperature resistant; the excess used may go as high as 125% in relation to the chlorocogazine, yielding monoalkyl naphthalene; i.e., each molecule of oil contains only one naphthalene group, despite the excess used. The yield of oil increases considerably under those conditions.

H. Koelbel cites the data given in Table 1.

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TABLE 1

Percent naphthalene in relation to cogazine	Yield of oil in relation to cogazine, in %	Viscosity at 50°C in E_o	Polar quantity	Conradson Number
0	32	5.0	1.87	1.4
33	78	15.48	1.91	0.78
66	105	13.52	2.01	0.74
83	112	13.83	2.06	0.62
104	119	15.09	2.12	0.62
125	122	13.04	2.12	0.60

The percentage relationship given here deviates considerably from that given in the sources used by Doctor Tokarzewski. In the sample calculation, however (Figure 1), Doctor Koelbel gives the amount of naphthalene as 66% of the amount of cogazine.

According to a Raman analysis the approximate composition of the synthetic oil was as follows:

30 to 35% β-alkylized naphthalene with 16 carbon atoms in the chain;

about 15% α-alkylized naphthalene with 16 carbon atoms in the chain;

10 to 15% $\alpha + \beta$-alkylized naphthalene with 6 to 9 carbon atoms in the chain;

one to 2% β-alkylized naphthalene with 6 to 9 carbon atoms in the chain;

0.5 to 1.0% α-alkylized naphthalene with 6 to 9 carbon atoms in the chain;

one percent isoparaffins

2% n-paraffins ranging from C_{16} to C_{18},

30% high-viscosity and high-molecular residue of an as yet undetermined composition.

The residue probably consists of dialkylized naphthalenes, dinaphthyl alkanes, and of high-molecular products of condensation.

An example of a distillation curve and of an analysis by the Raman method of the individual synthetic oil fractions is given in Figure 2.

The effects of the length of the side chains on the viscosity and on the Walther "m" coefficient, i.e., on the relation of viscosity to temperature, are shown in figures 3 and 4.

The amount of catalyst used is given by H. Koelbel as one percent, rather than 4%, computed in relation to the synthetic oil yield; the duration of the polymerization process is given as 15 minutes, rather than 3 to 4 hours. The composition of the catalyst and the method of its preparation has remained a secret of the inventor. Polymerization temperature is given as 80 to 100°C; the amount of solvent used (a

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150 to 220°C benzine fraction) is 200% in relation to the cogazine.

In the above example, the use of a solvent causes a drop in the viscosity at 50°C from 14.3 to 10.4 cSt and the Conradson Number drops from 1.78 to 0.48, but at the same time the oil yield goes up from 105 to 131%, in relation to the cogazine.

The use of a solvent reduces the amount of complex compounds (sludge) probably by reducing the amount of occluded oil; it also becomes easier to separate them quickly from the oil.

The following range of products is obtained:

15 to 20% of transformer oil
25 to 60% of turbine oil
25 to 60% of cylinder oil for superheated steam or bright stock.

The distillation range in an 0.05 mm Hg vacuum, converted to atmospheric pressures, was as follows:

about 20% from 230 to 430°C; 50% from 430 to 460°C and a 30% residue.

Table 2 gives the properties of the synthetic oils obtained by the Koelbel method.

Finally, Figure 5 presents a diagram of the industrial installations for the synthesis of lubricating oils by the H. Koelbel method.

The liquid chlorine from the storage tanks is vaporized, and it reacts with the cogazine at chlorinating installation 1 at a temperature between 60 and 100°C. The heat of reaction is removed by a circulating cooler, and the HCl produced is taken up through absorption. The chlorocogazine, naphthalene, solvent, and catalyst are introduced into reactor 3 through measuring devices 2, and the mixture reacts at the above temperatures. The HCl obtained is processed into hydrochloric acid. The choice of appropriate materials for the apparatus makes it possible to overcome the technical difficulties involved in dealing with large quantities of hydrogen chloride. The reaction is completed in 15 minutes. After brief settling of the complex compounds, they are removed. The synthetic oil solution is neutralized in distiller 4, and a small amount of bleach is added in order to remove any remaining complex compounds. The solution is then filtered on filter presses 5. The solvent and unreacted naphthalene are driven off in a column with a low degree of vacuum. The synthetic oil is pumped up to 7 for high-vacuum distillation and is separated into 4 fractions. The first fraction consists of unreacted and dechlorinated chlorocogazine, which is returned to the chlorination process. The second fraction has a boiling range from 340 to 415°C and corresponds to transformer oil; the fraction with a boiling range from 415 to 470°C corresponds to turbine oil; the fourth fraction constitutes the distillation residue, and is used as bright-stock oil for preparing mixtures for motor oils, or simply for use as cylinder oil. No additives are used to improve the viscosity index and the oxidation test. The plant produced 3,600 tons of synthetic oils per year and was to be expanded further.

Using a refined petroleum product with the same boiling range as the cogazine in place of the latter produces interesting results. The data of this test -- which turned out negative -- are given in Table 3.

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PROPERTIES OF SYNTHETIC OILS OBTAINED BY THE KOELBEL METHOD

	Trans-former oil	Turbine oil		Motor oil		Lubricant base oil for engines	Bright stock oil	
		light	heavy	winter	summer			
Specific gravity, d_{20}	0.907	0.894	0.921	0.929	0.930	0.902	0.895	0.912
Viscosity at 20°C, °	0.52	0.71	0.71	0.98	22.15	17.15	2.17	14.0
Cetane quantity	–	2.0	1.20	1.95	2.01	0.91	–	–
Solidifying point, °C	-47	-45			-16	-25		
Flash point, °C	170	260	280	205	250	239	320	331
Corrosion number:								
a. for iron, %	0.02	0.004	0.00	0.0	0.01	0.01	0.0	0.00
b. for cast iron	–	0.005	0.02	0.25	0.1	0.01	1.0	0.2
Acid number	0.0	0.0	0.0	0.0	0.00	0.00	0.00	0.0
Saponification value	0.1	0.1	0.1	–	–	–	–	–
Iod number	0.00	0.03	0.02	–	–	–	–	–
Resin number	0.00	0.02	0.07	–	–	–	–	–
Emulsifying test	–	Non-emulsifying		Non-emulsifying		–	–	–
Asphalt content	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.65
Ash content	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.01
Pleuring test, kG/cm [sic]	290							
Electric coefficient of losses at 50C and 20°, tan	1.7							
Dielectric constant	2.2							

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TABLE 3

Starting material	Refined petroleum product	Cogasine
Specific gravity, d_{20}	0.839	0.77
Boiling range	280-320°	280-320°
Chlorine content recomputed in terms of hydrocarbons	20.3%	20.9%
Properties of the lubricating oil:		
Specific gravity, d_{20}	0.96	0.92
Viscosity at 50°C, in E_o	8.2	11.98
Polar quantity according to Ubbelholde	3.7	2.0
Conradson number	1.4%	0.5%
Conradson number after aging	1.8	0.6
Solidifying point, °C	2.0	-25

The present writer nevertheless believes that a positive solution could be obtained to this problem.

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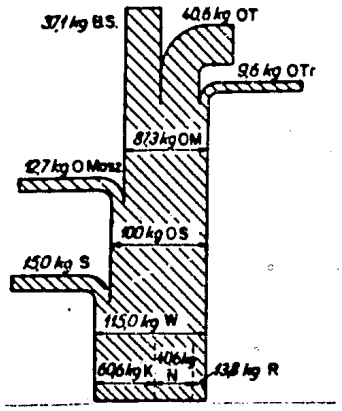

Figure 1. Example of a material balance in the synthesis of crude oil. BS, Bright Stock (cylinder oil for superheated steam); OT, turbine oil; OTr, transformer oil; OM, motor oil; OMasz, machine oil from catalysis; OS, lubricating oil; S, losses; W, hydrocarbons; K, cogazine; N, naphthalene; R, solvent.

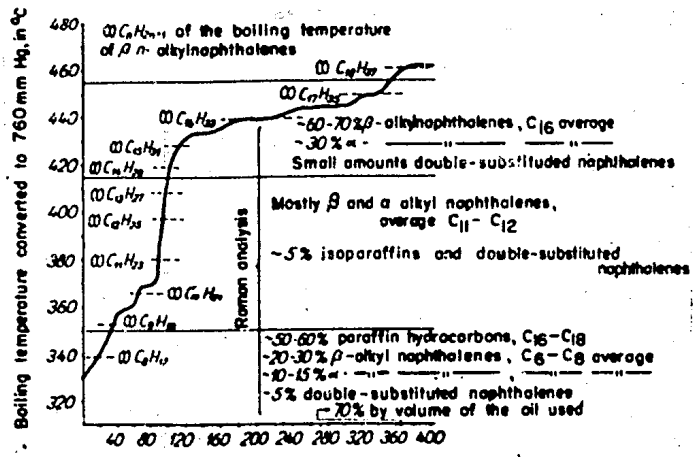

Figure 2. Distillation curve and Raman analysis of the synthetic oil.

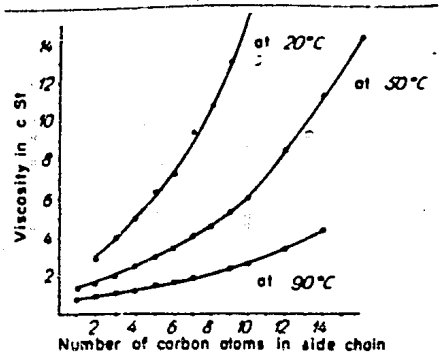

Figure 3. Relationship of viscosity to the length of the side chain in the homologous series of β-n-alkyl naphthalenes.

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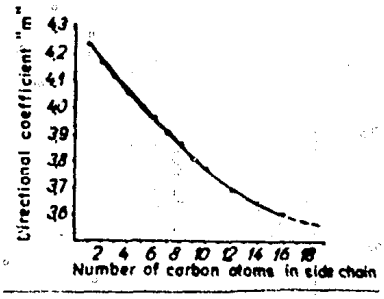

Figure 4. Relationship of Walther's directional coefficient "m" (of the viscosity-temperature curve) to the length of the side chain in the homologous series of β-n-alkyl naphthalenes.

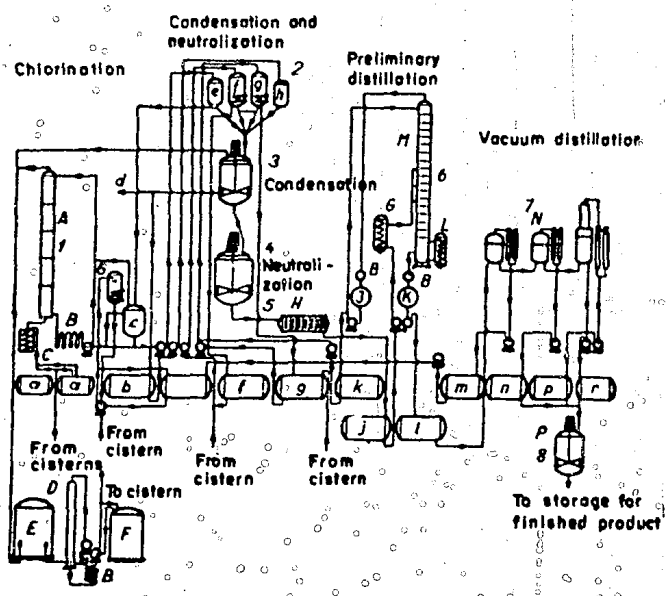

Figure 5. Diagram of the technical installations for the synthesis of lubricating oils. A, installation for chlorination; B, cooler; C, evaporator; D, absorption tower; E, collecting tank for gaseous HCl; F, tank for hydrochloric acid; G, heater; H, filter press; J, collector for slime; K, collector for basic oil; L, vaporizer; M, distilling column; N, distillation boilers; P, oil mixer; a, chlorine; b, complex compounds; c, chlorinated cogazine; d, complex compounds which are no longer used; e, chlorocogazine; f, naphthalene; g, solvent; h, catalyst; j, purified oil solution; k, returned solvent; l, basic oil; m, returned cogazine; n, transformer oil; p, turbine oil; r, cylinder oil for overheated steam.

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